High Throughput Screening of Nanostructured Hydrogen Storage Materials

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Hydrogen Storage: Challenges

Our Goals:
- Increase storage capacity
- Speed up transport (hydriding and dehydriding time)
- Study thermodynamics (to increase efficiency and improve thermal management)
- Study heat transfer

Heat Transfer Issues
- Hyriding reaction:
  ~1 MW for 5 min.
- Excessive temperature rise suppresses hydriding reaction.
Desirable range of binding energies: 10-60 kJ/mol (0.1 - 0.6 eV)

Physisorption
low T molecular H₂

Chemisorption
high T atomic H

Bond strength [kJ/mol]

Silica Aerogel

Berkeley

Chemical+Physical Sorption

H₂ uptake (wt.%) vs. pressure (bar)

25°C

Hydrogen uptake (wt.%) vs. pressure (bar)
Benefits of Nanostructures

- Increase kinetics: diffusion time ~ radius square/diffusivity
- Possibility of co-existence of chemi- and physi-sorption
- Possibility of changing thermodynamic properties

- **Yang’s Equation:**
  \[ p_i - p_o = \frac{2\sigma}{r} \]
  - Surface Tension
  - Radius

- **Kelvin Theory:**
  - For multiphase system, transition temperature, equilibrium pressure and enthalpy of reaction change with radius.
  - For hydride, we can expect similar dependence in release temperature, equilibrium pressure and enthalpy of formation.
Proposed Approaches

Key Strategies:

- Destabilize materials: nanostructures synthesized by laser pyrolysis
- Combinatorial synthesis: search large phase space
- Nanostructures for both chemi- and physi- sorption coexistence
- Size effects: to modify thermodynamics and transport
- Address thermal conductivity reduction at nanoscale
Teaming and Interactions

Team Members:
- G. Chen, mass and heat transport, thermodynamics
- M.S. Dresselhaus, electronic structure, physisorption
- C. Grigoropoulos, characterization, fabrication
- S. Mao, characterization
- X.D. Xiang, combinatorial synthesis
- T.F. Zeng, nanoporous structures

Collaboration
- Group meetings, Weekly at MIT and Berkeley
- Team meetings: physical (2) and teleconference (4)
- Individual visits, students exchanges
- Exchange of reports, meeting notes and research advances occurring elsewhere
- Daily email communication
Combinatorial Material Screening

Materials Fabrication

Proof of concept

Series Process vs. Parallel Process

(one at a time)  (up to a thousand at a time)

Metal and complex hydride materials

Combinatorial Nano-particle Discovery Engine™ (CNP)

- Capable of synthesizing nano-particles of metals, metal alloys and hydrides
- Reproducible high crystalline quality nanoparticles synthesized with narrow size distribution (< ±30%)
- Controllable process for combinatorial synthesis of nano-particle libraries with adjustable parameters:
  - particle size
  - material composition
  - synthesis conditions

Equipment at Intematix
Library of Nanoparticles with Narrow Size Distribution

Injection Rate (Frequency/Pulse Duration)

1Hz/0.5ms  2Hz/0.5ms  3Hz/0.5ms

Laser Power

130W  A1  B1  C1
190W  A2  B2  C2
230W  A3  B3  C3

Atomic imaging

50nm

Size Distribution (a.u)

Intematix

Other sources

Particle Size (nm)
Start: Mg-X-Y System

- High hydrogen storage capacity (MgH₂, 7.7 wt% H₂)
- Hydrogen release temperature (T_r) (1 atm H₂ at 300°C) provides enough range in T_r for destabilization while T_r is not too high for direct dehydrogenation
- Example: Literature shows some improvement by Ni destabilization (Mg₂Ni, 2.5-3.2 atm H₂ at 300°C)

Selected Candidates for X, Y
# Mg-Ni Metal Hydride Library

## Ni/Mg ratio

<table>
<thead>
<tr>
<th>Ni/Mg ratio</th>
<th>Laser power (W)</th>
<th>C₂H₄ Flow (sccm)</th>
</tr>
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<tbody>
<tr>
<td>2:1</td>
<td>250</td>
<td>50</td>
</tr>
<tr>
<td>1:1</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>1:1.5</td>
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<td>100</td>
</tr>
<tr>
<td>1:2.5</td>
<td>250</td>
<td>100</td>
</tr>
</tbody>
</table>
MgH$_2$ in Aerogel Form

- Incorporation of MgH$_2$ into a nanoporous silica aerogel increases diffusion and prevents particle sintering
- Possibility of simultaneous chemi- and physi- sorption

- Synthesized silica aerogel with surface area 1,100 m$^2$/g
- Modified a well established aerogel synthesis route to prevent MgH$_2$ decomposition
- Incorporate nanoscale catalyst into aerogel
- Also used laser to deposit MgNi into aerogel
Screening of Combinatorial Library

- X-ray analysis
- Infrared Imaging
- Pump-and-Probe
- Cantilever Arrays

Change in natural frequency of oscillation offers direct measurement of hydrogen intake.
IR Imaging

Before

After
Pump-and-Probe Technique

Properties of interest: (a) thermal conductivity, (b) specific heat
Differential Scanning Calorimetry

MgH₂ aerogel

468.9 °C

MgH₂ + catalyst 1 aerogel

475.3 °C

MgH₂ + catalyst 2 aerogel

466.8 °C

MgH₂ + catalyst 3 aerogel

456.3 °C

Study of enthalpy of formation and activation temperature for different catalysts

Commercial MgH₂ Particles

Area = 23471.197 mJ
Delta H = 5942.075 J/kg

Intematix
Resonant Inelastic X-ray Spectroscopy (RIXS) used to excite specific core electrons (a, b, c, etc. from XAS plot).

Some small differences were noted after hydride formation, but spectra strongly resemble NiO (J. Phy. Soc. Japan, 70, 1813)

Need to repeat experiment with pure samples for more accurate results.

DOE User Facility, ALS at LBNL
In-Situ Deposited MgNi

- Laser pulse
- Expanding metal vapor
- Nanoporous sample
- Target material

Graph showing hydrogen uptake (wt.%) against pressure (bar) with various markers indicating different sorption and desorption processes.

- MgNi:SiO\textsubscript{2} sorption
- MgNi:SiO\textsubscript{2} desorption
- MgNi:SiO\textsubscript{2} sorption (7 days)
- MgNi:SiO\textsubscript{2} desorption (7 days)
- SiO\textsubscript{2} sorption
- SiO\textsubscript{2} desorption (7 days)
• Diffusion limited hydride reaction.

• Optimal pore and particle sizes: balance pore diffusion and diffusion in the solid particle to control kinetics.

• The strongly exothermic hydriding reaction increases the sample’s temperature which reduces the reaction rate or even stops the reaction altogether.

• Rapid hydriding reaction thus requires effective heat removal solution.

• Nanostructures usually have poor heat transfer characteristics. Therefore, we need to balance mass diffusion kinetics with heat transfer.
Assuming the following reaction

\[ M + H_2 \rightarrow MH_2 \]

- At nanoscale, surface and size affect reaction enthalpy.
  - Increase the surface to volume ratio.
  - Increase adsorption sites due to low coordination surface atoms.
  - Lower binding energy in small metallic clusters.

\[ \Delta G = \Delta G_o + RT \ln\left(\frac{a_{MH}}{a_{M}P_{H_2}}\right) \]

Van’t Hoff relation

\[ \ln P_{H_2}^{eq} = \frac{\Delta H_o}{RT} - \frac{\Delta S_o}{R} \]

Nanoparticle molar free energy of formation

\[ \Delta G(r) = \Delta G_o(r) + RT \ln\left(\frac{a_{MH}}{a_{M}P_{H_2}}\right) \]

\[ + \frac{3V_M \Delta M\rightarrow MH(r)}{r} \]

\[ \Delta_{M\rightarrow MH}(\gamma, r) = (\gamma_{MH}(r)\left(\frac{V_{MH}}{V_M}\right)^{2/3} - \gamma_M(r)) + E_{adsorption} \]
Modeling DFT Results

- If internal energy dependence on radius is all contained in the surface energy term

\[ \Delta E(r) \approx \Delta E_{Bulk} + \frac{3V_M \Delta_{M\rightarrow MH}(\gamma, r)}{r} \]

- Following Tolman’s work, surface tension is allowed to vary with radius

\[ \Delta = \frac{\Delta_o}{1 + \frac{a}{r}} \]

DFT values of internal energy calculated by Wagemans et al.
\[ \ln \left( P_{H_2}^{eq} \right) = \frac{\Delta H^o}{RT} + \frac{3V_M \Delta M \rightarrow MH}{rRT} - \frac{\Delta S^o}{R} \]

\[ \Delta H_{\text{eff}} = \Delta H^o + \frac{3V_M \Delta M \rightarrow MH}{r} \]

- Nanoparticles with positive \( \Delta \) will have
  - Lower equilibrium temperature
  - Less heat release during hydrogenation
Major Work Carried Out Since 09/05

1. Synthesis
   - Synthesized Mg-Ni libraries
   - Incorporated metal hydrides into aerogel

2. Characterization
   - Developing fast characterization tools
   - Aerogel + MgNi sorption and desorption data suggests simultaneous physi- and chemi-sorption
   - Synchrotron XAS and XES analysis of samples

3. Modeling
   - Theoretical studies of size effects on transport and thermodynamics
Future Plan

1. Synthesis
   - Improve laser based synthesis method
   - Continue synthesis of Mg-X-Y library and other libraries
   - Incorporate hydride nanoparticles in aerogel
   - Developing nanoporous composites of nano-catalysts along with hydride nanoparticles

2. Characterization
   - Continue developing characterization tools (IR, XAS, XES, pump and probe, cantilever analysis)
   - Continue characterizing samples

3. Modeling
   - Continue developing transport and thermodynamics models, and incorporate heat transfer considerations
   - Carry out first principles calculations to study the effect of size on key parameters